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# Layer-by-Layer Coating of Oriented Conjugated Polymer Films towards Anisotropic Electronics

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## **Abstract**

Dynamic casting of floating-film and transferring method for preparing oriented multilayer films of conjugated polymers is reported. This method is based on dynamic casting of a floating-film on liquid substrate to obtain oriented thin-film followed by its transfer on a desired solid substrate. The uniqueness in this method lies in the isolation of casting and coating procedures of oriented films, which enables us to fabricate the oriented multilayer with minimum interlayer interference. It provides a key-technology to build up the organic multi-layered architecture while preserving oriented morphologies. Several types of multilayer films have been prepared and investigated in detail in terms of their film characteristics. The layer-by-layer coating of oriented films demonstrated by this method is found to be a unique feature which overcomes cumbersome procedures in the conventional orientation methods. The coating procedure demonstrated in this study provides a facile methodology to construct anisotropic architectures.

# 1. Introduction

Solution processed semiconductor thin film is one of the important features for organic electronics which enables us for large scale and facile fabrication of thin film photonic and electronic devices. Device performance strongly changes with the film morphology of the semiconductor layer [1-3]. The casting procedure of semiconductor layer from solution is, therefore, the key-technology to fabricate organic electronic devices. Drastic change in the organic device performance is essentially caused by the anisotropic structure of conjugated molecules and polymers [4-7]. The molecular alignment is, therefore, very important to induce the potential performance for organic semiconductors. Conjugated polymers are structurally the most anisotropic organic semiconductors due to their one-dimensional expansion of conjugation on main-chain. In the recent past, amorphous film formation has been favored for reproducible electronic performance due to its uniform characteristics [8]. Currently, however, it has been realized that high transport performance is required in semiconductor even with the existence of anisotropy in carrier transport [5-7]. This offers a strong urge for suitable thin film fabrication processes capable of promoting the alignment of macromolecules in order to attain enhanced device functionality.

Molecular ordering is essentially required to improve the intermolecular transport for organic semiconductors, where drop-casting is thermodynamically favorable to attain this goal [9]. Drop-casting of semiconductor-solution directly onto the device substrates, however, sometimes results in to partial bumps (islands) or non-uniform thickness, which is supposed to be originated from pinning effect or coffee-ring effect by the solution-solid substrate interactions

[10]. Due to the large volumetric reduction during solvent vaporization, discrete solidification results in to the failure of uniform thin-film formation on the solid substrate. In such process, if the substrate surface can move to provide the chance for joining the solidifying parts together it will promote to cast a uniform thin-film. This indicates the importance of utilization of “liquid-or fluid-substrate” for drop-casting process. In the case of hydrophobic semiconductor solution, hydrophilic materials such as water, ethylene glycol and/or glycerol can be utilized as the liquid-substrate for the casting. On liquid-substrates, we obtain the organic semiconductor thin-film as a floating-film after the solvent evaporation, which can be easily transferred on a desired substrate by stamping. The procedure for casting a thin floating-film followed by its transfer on desired substrate can be expressed as floating-film transfer method (FTM) [11].

Gradually vaporizing solvent after the expansion of dropped semiconductor solution on the liquid-substrate semi-statically provides a floating-film in FTM (represented as static-FTM). In contrast, simultaneous solidification of the floating-film along with the expansion of the semiconductor solution is dynamically occurred just after dropped on the liquid surface (represented as dynamic-FTM), leading to a concentric orientation of conjugated polymers. Poly(3,3',4,4'-dialkyl-quaterthiophene) (PQT) as well as polyfluorene derivatives can easily oriented by this procedure [12]. The solvent volatility of semiconductor solution, generally, identifies the types of FTM. Namely, under ambient condition static-FTM occurs after the complete expansion of semiconductor solution utilizing high boiling point solvents like chlorobenzene because of their slow evaporation. In contrast, for dynamic-FTM semiconductor solution prepared in the relatively low boiling point solvents (such as chloroform, tetrahydrofuran and dichloromethane) leads to simultaneous film expansion and solidification [13].

Casting of thin-films at the air-liquid interface proceeds under isothermal condition like Langmuir-type methods have been studied and developed by many researchers [14]. Introduction of liquid-crystal molecules with conjugated polymer successfully forms transversally oriented films where thin-film is formed by applying surface pressure in Langmuir isotherm [15]. In contrast, in the dynamic-FTM self-caused motion of liquid substrate and/or semiconductor solution spreading on the liquid-substrate, casts a thin floating-film automatically. These differences suggest that FTM process should be characterized little apart from the Langmuir process in spite of their methodological analogy.

Transverse orientation methods of conjugated polymers also have been developed and investigated by many researchers [16]. In these reports, fine orientation of conjugated polymers at micrometer-scale along with the demonstration of high optical and electronic dichroism. Most of these methods prepare oriented films directly on the device substrate, for example, mechanical rubbing, friction transfer and flow-coating with post-annealing [17-19]. These methods essentially require various chemical, mechanical or thermal stimuli for the promotion of macromolecular orientation. At the same time, these stimuli provide mechanical and/or chemical damages on the coated-surface, in particular, the surface consisted of soluble or soft organic materials. This makes it impossible to build up organic multi-layered fine structure, which is a bottleneck for the application of in particular oriented functional layers into organic electronic devices.

FTM is essentially consisted of the two-step processes, namely to pre-cast an oriented thin-film as solution process followed by the post-transfer of the film on the solid substrate like a dry process. The isolation of the orientation process from the coating process enables us to

overcoat the oriented film on any surface without chemical or mechanical damages. In particular, conjugated polymer acts as active layer for photonic and electronic devices. As already mentioned above the device performance is sensitive to the film morphology as well as the film purity. Thus, a mild coating procedure of organic semiconductor-layer with conserving the oriented film-morphology and without the mixture of organic semiconductor with under-lying other materials is strongly required for fabricating organic devices consisted of multi-layered fine structure. In this context, FTM as the solution-based casting procedure provides a mild coating while maintaining the purity as well as the morphology both in the under-coated and the over-coating layers. Figure 1 shows a schematic illustration of the dynamic-FTM.

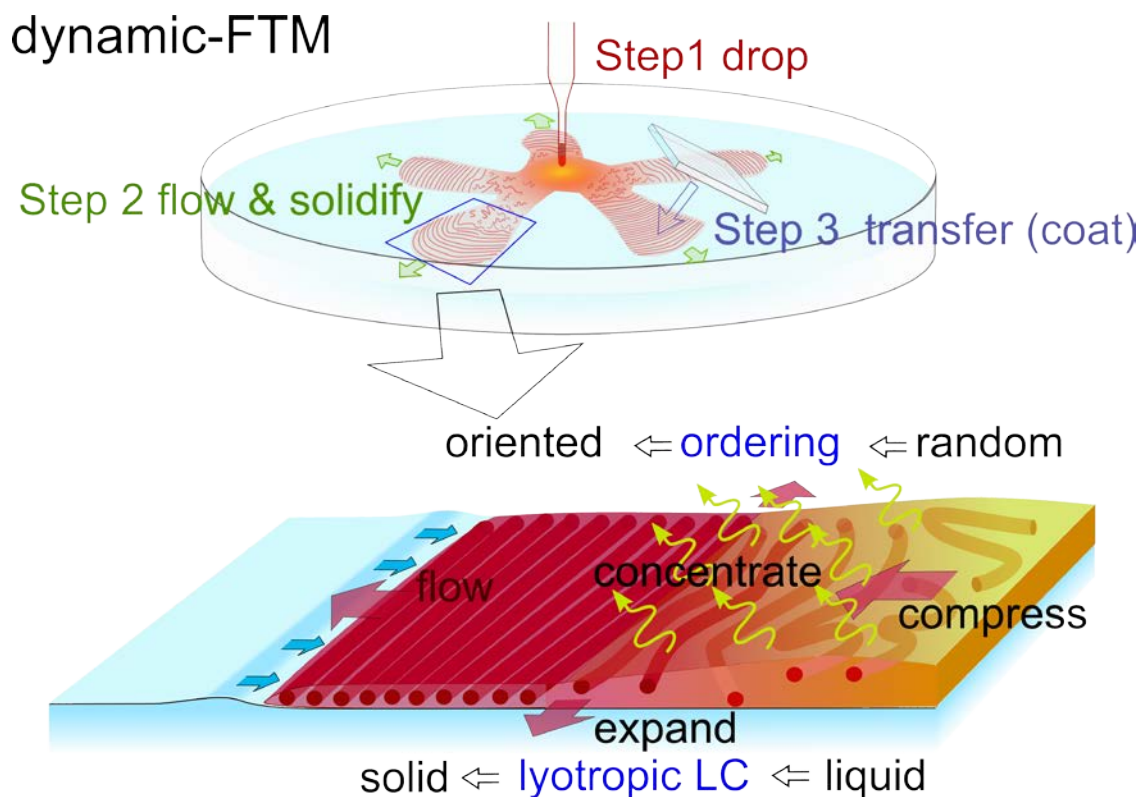


Figure: 1. Schematic illustration of the overview of dynamic-FTM (upper) and a possible mechanism to cause the orientation (lower) during casting.

Recent past has witnessed the design and development a variety of conjugated polymers in order to provide the tailored functionality [20-22]. For analyzing newly synthesized materials, spectroscopic characterizations are very powerful way to clarify the chemical structure at molecular level. The polarized analyses of the oriented film provide further details about the structural information together with non-polarized spectra. A quick casting method to prepare the oriented thin-film with minimal materials wastage is, therefore, very useful for the material characterization utilizing polarized spectroscopy.

In this article, we propose dynamic-FTM as one of the candidates to prepare the multi-layered films consisted of oriented polymeric materials. The oriented multi-layer formation renders the realization of anisotropic electronics into the practical devices [23-24]. The proposed dynamic-FTM is not only simple and quick oriented film casting procedure but also leads to the utilization of small amount of the materials with minimum wastage. In this study, we investigated the orientation characteristics of dynamic-FTM films with conjugated polymers. Efforts have also been directed towards the preparation and characterization of multi-layered oriented films of conjugated polymers fabricated using dynamic-FTM.

## **2. Experimental**

All of the chemicals and the reagents employed in this work are used without further purification. Three types of conjugated polymers, viz. non-regiocontrolled poly(3-hexylthiophene) (NR-P3HT) [25-26], poly(3,3-didodecylquaterthiophene) (PQT) [27] and poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) [28], were synthesized as per the reported procedures. Chemical structures were identified by  $^1\text{H-NMR}$ . In particular, the regioregularity of



NR-P3HT was estimated at  $\alpha$ -methylene region in  $^1\text{H}$ -NMR spectra [29]. Major emphasis in this study has been directed with NR-P3HT as the main polymer due to the fact that it is easy to prepare well-oriented floating-film and to check the orientation intensity simply by the naked eyes through a polarizer-film easily [5]. Typically, 10 mg of polymer powder was dissolved in 1 ml of dehydrated chloroform to obtain a uniform 1 % (wt/wt) semiconductor solution.

Hydrophilic liquids such as water, ethylene-glycol and glycerol were chosen for the materials of liquid-substrate to cast floating-films. Solvents were well-mixed at an appropriate mixing ratio in order to tune the viscosity of the liquid substrate and temperature was also optimized for obtaining the high orientation [30]. The mixture was poured in a 15 cm-diameter petri-dish, stirred and controlled at a suitable temperature. The dynamic-FTM was carried out by putting single droplet (about 10-20  $\mu\text{l}$ ) of semiconductor solution at the center of liquid-substrate without touching the pipette on the liquid-surface. After the semiconductor solution quickly spread and formed a floating-film, it kept drying for about 20-30 seconds. A fairly oriented part of the floating-film was selected and transferred on a solid substrate by stamping similar to Langmuir-Schaefer method. The transferred film-surface was washed with methanol followed by air blowing. Thickness of single layer film was found to be about 20-30 nm as confirmed optical non-contact surface profiler. Spin-coated films of NR-P3HT were also prepared for comparison. Multiple parallel-coatings were conducted for the fabrication uniaxially oriented films in the similar way as described above. For the polarized film characterizations about 50 times parallel-coatings have been done in order to obtain a thick-oriented film of about 0.75  $\mu\text{m}$  for analysis. A thick spin-coated film was also prepared from the 2.5 % (wt/wt) semiconductor solution at 1500 rpm for 120 second to obtain 0.70  $\mu\text{m}$  thick film for the comparison.

Transparent white-glasses were used for polarized absorption spectroscopy. Suitable size of pure Si-wafer pieces were coated NR-P3HT by FTM and subjected to thickness measurement, Fourier transform infra-red (FT-IR) spectroscopy, atomic force microscopy (AFM) and X-ray diffraction analyses. Si-wafer surface was treated with hexamethyldisilazane for the good adhesion of floating-films. Polarized absorption spectra were measured through a Glan-Thomson polarizing prism with Jasco V-570 spectrophotometer. FT-IR spectra were measured through a polarizer unit with Jasco FTIR-4100. Film thickness was estimated with Nikon Eclipse LV150. X-ray profiles were obtained by  $\theta$ -2 $\theta$  diffractometry with Rigaku Smart-Lab in both of the out-of-plane and the in-plane glazing incidence X-ray diffraction (GIXD) measurements. Dichroic ratio (DR) has been taken as the index of orientation intensity and estimated by the ratio of absorption maxima in the case of parallel and perpendicular-polarized absorption spectra as per our earlier publication [30].

### 3. Results and Discussion

#### 3.1 Absorption spectra of oriented single-layer film

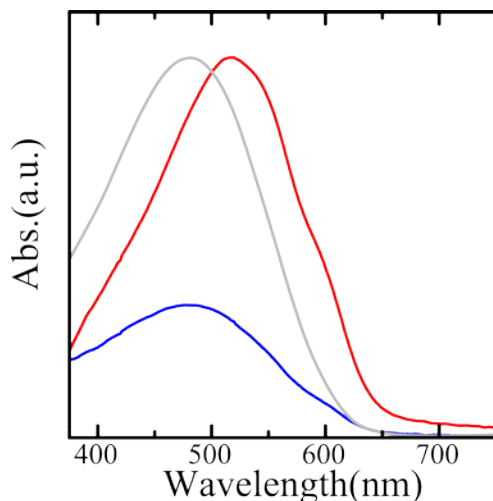


Fig. 2. Polarized electronic absorption spectra of FTM (parallel: red, perpendicular: blue) and spin-coated (gray) films of NR-P3HT. Spin-coated film spectra were normalized with respect to its peak absorption for the comparison of their spectral shape.

Fig. 2 shows the polarized electronic absorption spectra of each FTM and spin coated films where spin-coated films of NR-P3HT exhibit a featureless absorption spectrum having absorption maximum at 480 nm. This main absorption peak has been assigned to the electronic absorption associated with the amorphous phase [31-33]. This indicates that the NR-P3HT intrinsically forms an amorphous-rich film by spin-coating. On the contrary, for NR-P3HT parallel-polarized absorption spectrum of oriented film shows the main peak at 525 nm, which is strongly red-shifted as compared to the spin-coated one. Vibronic shoulders were also clearly observed around 550 nm and 600 nm. The absorption spectral profile of parallel oriented FTM films of NR-P3HT is almost similar to that of RR-P3HT films [31]. The vibronic shoulders at 550 nm and 600-610 nm are assigned to the 0-1 and 0-0 vibronic transitions, respectively, and their appearance suggests the presence of well-expansion of  $\pi$ -conjugation length [34]. This indicates that FTM effectively stretches NR-P3HT macromolecules like RR-P3HT in spite of their low regioregularity (~80%).

A different spectral profile was observed in the perpendicular-polarized absorption spectrum of oriented NR-P3HT film having optical DR of 3.5. Although weak vibronic shoulders are seen in the perpendicular spectra, the mismatch in the spectral shapes between this and the parallel one has been attributed to the still existence of amorphous region in the film as non-oriented part [13]. A similar spectral mismatch was also reported in the oriented RR-P3HT films also although the origin of the spectral mismatch has not yet been clearly discussed and clarified [18, 35]. It should be noted that PQT as well as other thiophene-based conjugated

polymers such as poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) also shows similar vibronic spectra [19].

### 3.2 Characterization of parallel-coated multi-layered NR-P3HT films

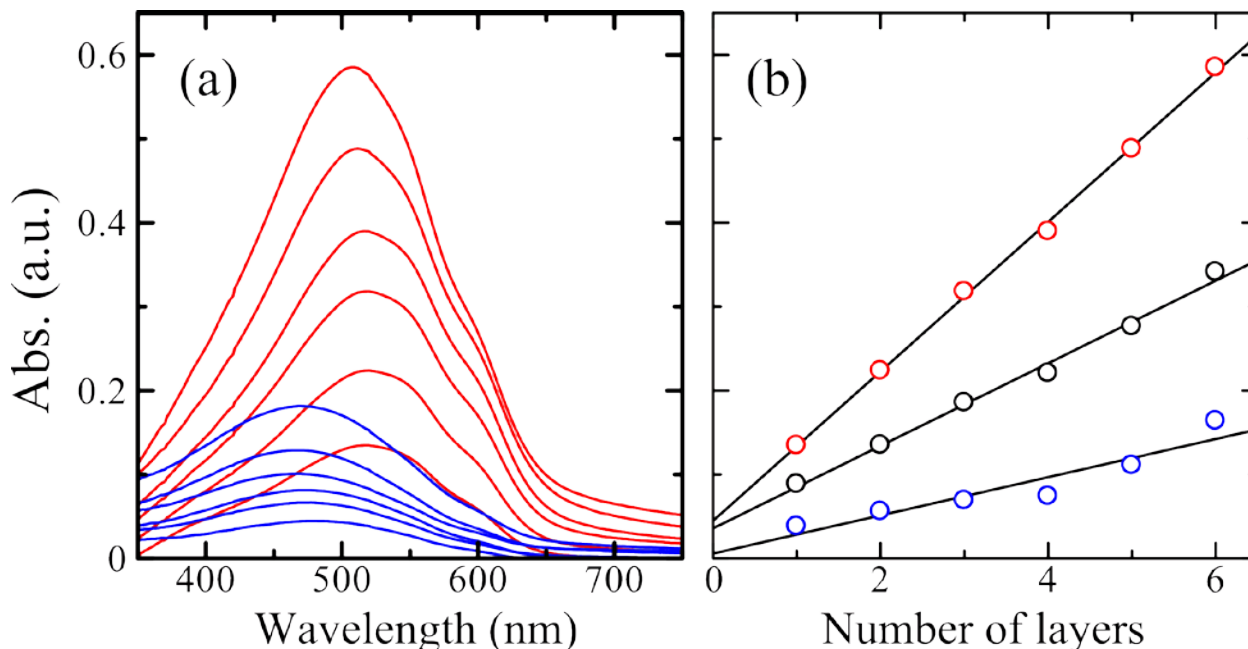


Fig. 3. (a) Evolution of polarized spectra with layer-by-layer coating in parallel direction and (b) peak height as a function of layer numbers in oriented NR-P3HT films. Red, blue and black colors represent the peak-height of the parallel-, perpendicular- and non-polarized ones at about 520 nm vibronic peak, respectively. Each polarized spectra in (a) can refer the number of layers in (b) adjusted with the peak height of absorption.

Fig. 3(a) shows the evolution of polarized absorption spectra of oriented NR-P3HT films with layer-by-layer coating in parallel direction by dynamic-FTM. As can be seen, the intensities of absorption peak in both the polarized spectra were found to be increased as a function of increasing layer number. In spite of the repetitive manual coating from the oriented region of floating-film, similar DR was maintained for each layer coatings. All of the parallel- or perpendicular-polarized spectra consistently show very similar profiles, indicating that all of the coated layers have similar orientation morphology. The linear relationship of the peak height of

non-polarized spectra found as a function of layer number as shown in Fig 3(b) represents that each layer has a similar thickness and this is similar to that of non-oriented multi-layer coating by Langmuir process. The linear relationships in both of the parallel- and perpendicular-polarized spectra also imply that DRs in all the coated layers are almost the same. This fact enables us to prepare various thickness of oriented film by multiple about 20 nm-thick single layers. At the same time the dynamic-FTM provides over-coating of an oriented film without interlayer-interferences.

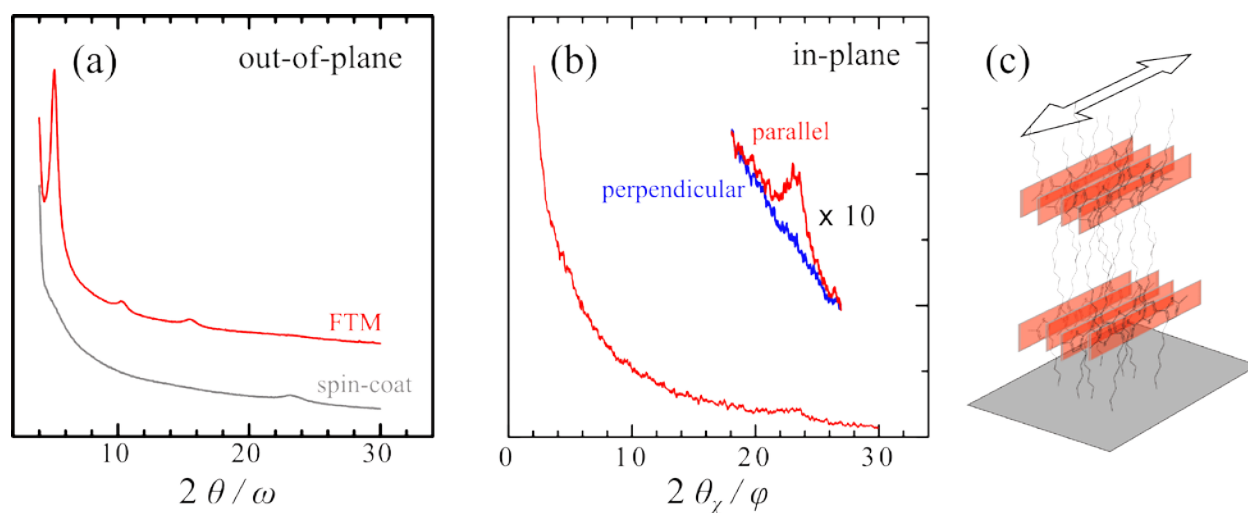


Fig. 4. X-ray diffraction profiles of spin-coated (gray) and parallel-coated multi-layer (red/blue) films of NR-P3HT. (a) out-of-plane and (b) in-plane (red: parallel; blue: perpendicular) profiles. (c) Schematic drawing of the structural orientation of P3HT macromolecules according with (a) and (c). Black arrow represents the orientation direction of main-chain.

Fig. 4. compares the X-ray diffraction profiles of NR-P3HT films prepared by spin coating (0.70  $\mu\text{m}$ ) and multilayer parallel FTM (0.75  $\mu\text{m}$ ). In the out-of-plane profiles, the oriented multi-layer film shows clear diffraction peaks at 5.1 (1 0 0), 10.3 (2 0 0) and 15.5° (3 0 0). Contrary to this, spin-coated film shows only a broad peak at 23.0° (0 2 0). The former three peaks are assigned to lamellar structure attributed to the side-chain stacking, and the later as  $\pi$ - $\pi$

stacking of P3HT macromolecules, respectively [18, 36]. These differences in the XRD profile indicate that in the oriented multi-layer film, macromolecules stand on the substrate with side-chain as edge-on orientation as also illustrated in Fig. 4(c). On the other hand, macromolecules lie on the substrate in the face-on orientation for the spin-coated films, which is also reported in the literature [9].

In the in-plane (GIXD) diffraction profiles, all the (h 0 0) peaks disappeared in all the spin-coat, parallel and perpendicular directions. Instead of this, the oriented NR-P3HT film shows only  $\pi$ - $\pi$  stacking peak-profiles towards parallel direction (red in Fig.4 (b)). This  $\pi$ - $\pi$  stacking peak also disappeared in the perpendicular direction (blue in Fig.4 (b)). These in-plane profile characteristics further support that NR-P3HT, macromolecules stands as edge-on structure in oriented FTM films as illustrated schematically in Fig.4(c).

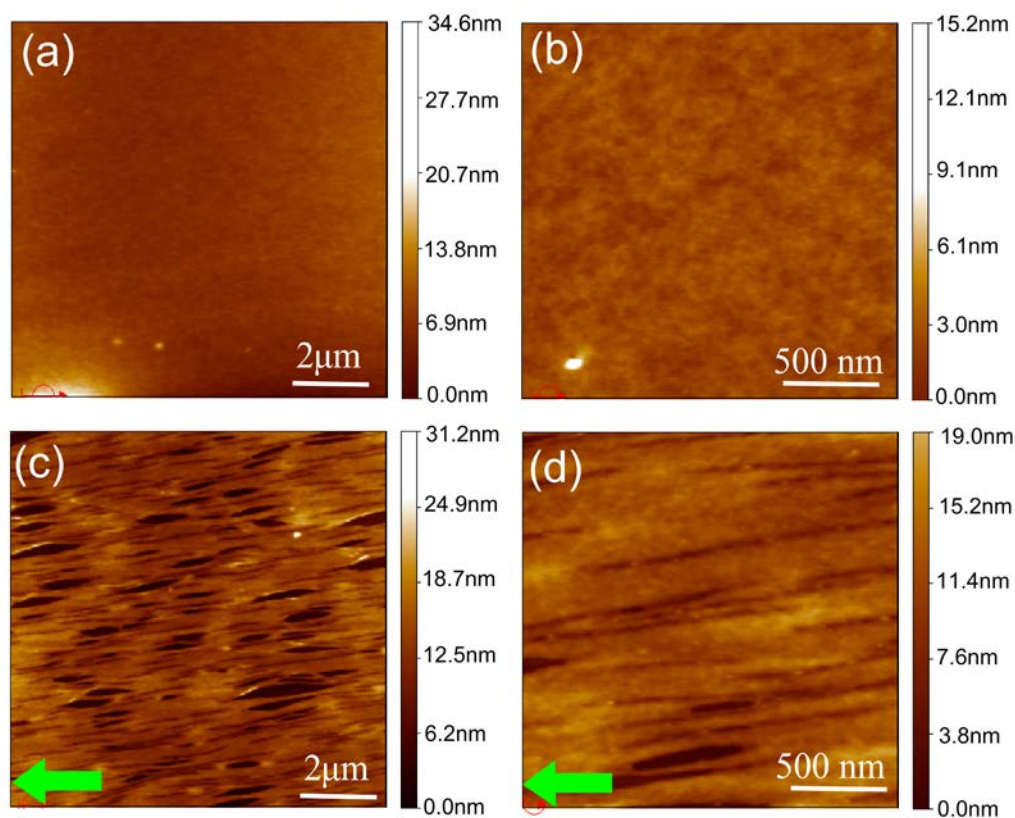


Fig. 5. Tapping mode AFM images. (a), (b) are of spin coated and (c), (d) are of oriented FTM films of NR-P3HT. Green arrow in (c) and (d) represents the direction of orientation.

Fig. 5 compares AFM images for both of the spin-coated and the oriented NR-P3HT films prepared by dynamic-FTM. A featureless flat surface was observed in the spin-coated film as shown in Fig 5 (a) and (b). In contrast to this clear stretched nano-size corrugations are aligned to the same direction over the surface as shown in Fig. 5 (c) and (d). The observed stretched direction in the AFM images is matched to the orientation direction of main chains visualized optically as well as through polarized absorption spectroscopy discussed in the beginning.

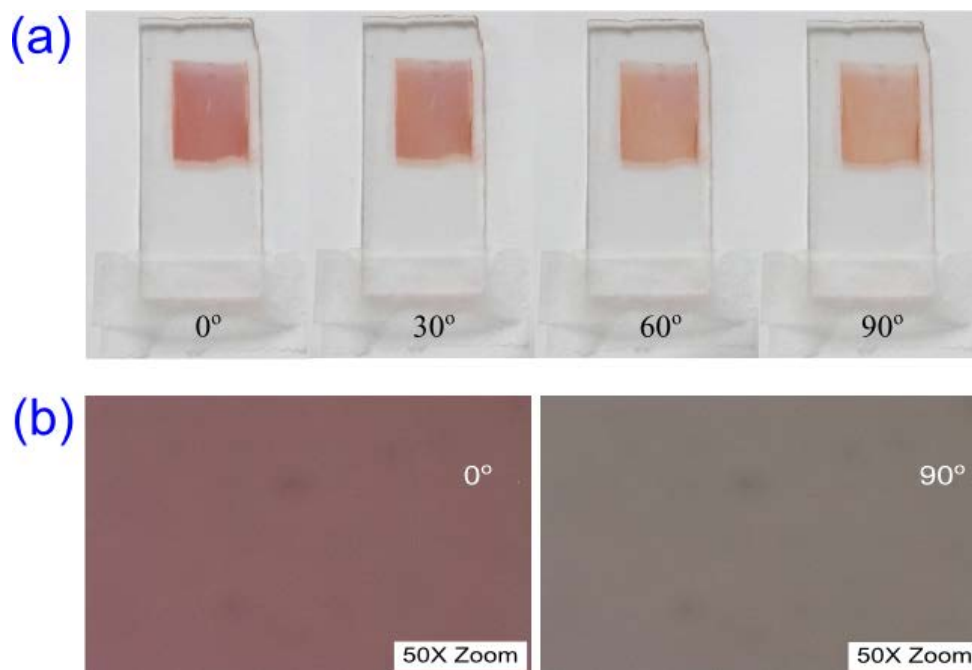


Fig. 6. (a) Photographs of a 5-layered oriented NR-P3HT film coated on a white glass (1cm width and 2 cm height) taken through a polarizer. Polarized angles based on the oriented axis are  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$  and  $90^\circ$  from the left to the right ones, respectively. (b) Polarized Microscopic Images at  $0^\circ$  and  $90^\circ$ .

Fig. 6 (a) shows the photographs of parallel-coated 5-layer films on glass substrate taken through a polarizer. A perusal of the photographs clearly corroborates that original reddish color of NR-P3HT is faded into orangey color as a function of polarized angle. These photographs represent that whole the coated layer orients almost into the same direction at this macroscopic scale. Dynamic-FTM enables us to cover whole of the centimeter-size substrate with various thicknesses. These facts draw us the quick analysis of anisotropic characteristics of  $\pi$ -conjugated polymer by standard equipment with simple polarizer, and also the easy incorporation of oriented semiconductor layers into organic devices. In addition, to consider both of the surface morphology of the oriented NR-P3HT film observed with AFM and the homogenous polarized color change of the film shown in the Fig. 6 (a), the stretched nanoscale objects are continuously



aligned throughout up to several centimeters. This means that about 4- or 5-order of magnitude scale orientation of these nano-structures prevails in the whole film. This is also one of the important features of dynamic-FTM to prepare a large (at least centimeter)-scale oriented  $\pi$ -conjugated polymers. This difference in color contrast has been also observed when this was subjected to polarized optical microscopy as shown in Fig. 6 (b). The small spot present in the POM images are basically due some stain in the lens.

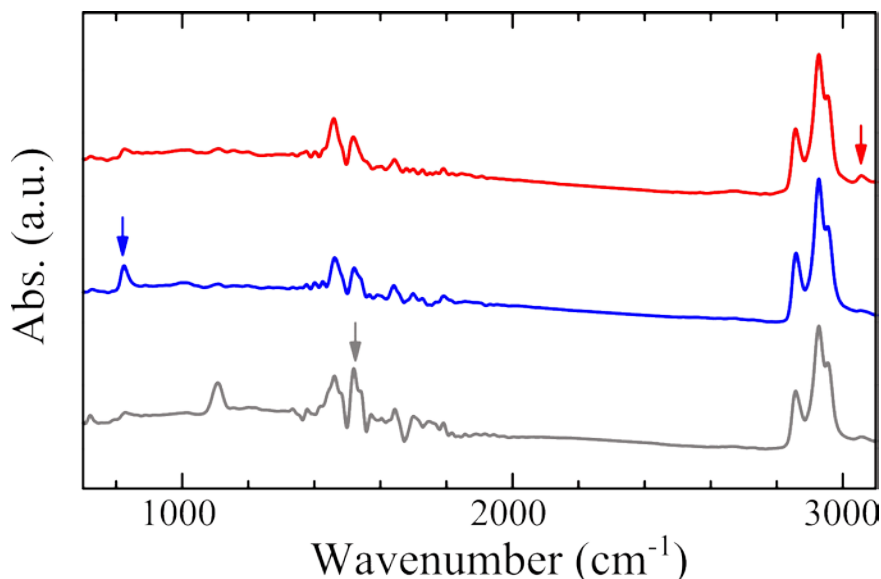


Fig. 7. FT-IR absorption spectra of NR-P3HT films. Red and blue lines are parallel- and perpendicular-polarized spectra of a parallel-coated multilayer (about 50-layer) film, and gray line is non-polarized spectra of a spin-coat film, respectively. Red-arrow at 3059  $\text{cm}^{-1}$ , blue-arrow at 823  $\text{cm}^{-1}$  and gray-arrow at 1517  $\text{cm}^{-1}$  are guided for the featured peaks in each FTIR spectrum.

Fig. 7 shows the (polarized) FT-IR absorption spectra for spin-coated and parallel-coated multi-layer NR-P3HT films. Although all the spectra essentially exhibit similar profiles but their detailed comparison clarifies the several differences in absorption band and its intensity. The parallel-polarized spectrum exhibits enhanced intensity at 3059  $\text{cm}^{-1}$  (red-arrow) as compared to that of the perpendicular-polarized one [37]. This is assigned as C-H stretching mode in thiophene-ring. In contrast, CH-out-of-plane deformation mode at 823  $\text{cm}^{-1}$  (blue-arrow) shows a

clear inverse dichroism [37]. The apparent contrast of these two peaks clearly supports the uniaxial orientation of P3HT main-chain.

It is interesting to note that the stretching vibration at  $1517\text{ cm}^{-1}$  (gray arrow) related to antisymmetric modes of thiophene-ring [38] get enhanced in spin-coat (amorphous-rich) film. The perpendicular-polarized spectrum (blue line), intensity of the vibration bands at  $1458\text{ cm}^{-1}$  is found to be relatively reduced than that at  $1517\text{ cm}^{-1}$  as compared to that in parallel-polarized spectra. These correlations are well-corresponded to the assignment of electronic absorption peaks as already discussed above with Fig. 2. Namely, the amorphous-rich film shows the relatively enhanced absorption at 480 nm in Fig. 2 and the  $1517\text{ cm}^{-1}$  vibration band in Fig. 7, coincidentally. It should be noted that expansion of  $\pi$ -conjugation has been correlated with the intensity of  $1517\text{ cm}^{-1}$  against  $1458\text{ cm}^{-1}$  based on FT-IR spectral investigations for a series of thiophene oligomers [37, 39, 40]. This seems to be contradictory compared to the result shown in the Fig. 7. In P3HT, since all the thiophene-rings are connected at both ( $\alpha$ - and  $\delta$ -) sides, strong stresses applied on the thiophene-ring. Amorphous structure enhances these stresses on the ring, which evidences the chemical connection of many thiophene-rings as the extrapolative structure in the series of thiophene-oligomers. Against this, in the crystalline phase of P3HT many thiophene-rings form as the trans-configuration of main-chain. This reduces the double side stresses and rather an isolated mechanical effects for the thiophene-rings. Such effects will increase  $1458\text{ cm}^{-1}$  with decreasing  $1517\text{ cm}^{-1}$  from amorphous-rich to crystalline rich domains.

It should be noted that in order to obtain the polarized FT-IR spectrum as well as GIXD profiles, a thick film (about  $1\mu\text{m}$ ) is commonly required for the orientation analysis by using standard equipment [37, 41, 42]. Dynamic-FTM can easily provide oriented thick film simply by

multiple parallel-coatings with small amount of the materials. For dynamic-FTM single drop (about 10  $\mu\text{l}$ ) of the semiconductor solution casts around 10-25  $\text{cm}^2$  floating-film. Several parts from single floating-film can be transferred for parallel-coating of oriented films. About 5 times of parallel-transfer can be easily done to coat well-oriented layers on the solid substrate from single floating-film. Commonly 1% (wt/wt) semiconductor solution is used for dynamic-FTM. This indicates that 1 mg of  $\pi$ -conjugated polymer dissolved in 100 mg of chloroform renders coarsely 50 layers for parallel-coating. This layer-number is enough to prepare an oriented thick-film for device fabrication as well as for film characterizations. In addition, these coatings can be carried out with common laboratory apparatus such as pipet, petri-dish, hydrophilic liquid and solvent and very small amount of target polymer. Therefore, the macroscopic orientation, ease in fabrication, parallel-coatings as a thick uniaxially oriented film prepared by small amount of the materials in dynamic FTM becomes the key-technology for polarized characterization of synthetic materials for chemical analysis.

### 3.3 Orthogonal coatings of oriented $\pi$ -conjugated polymers

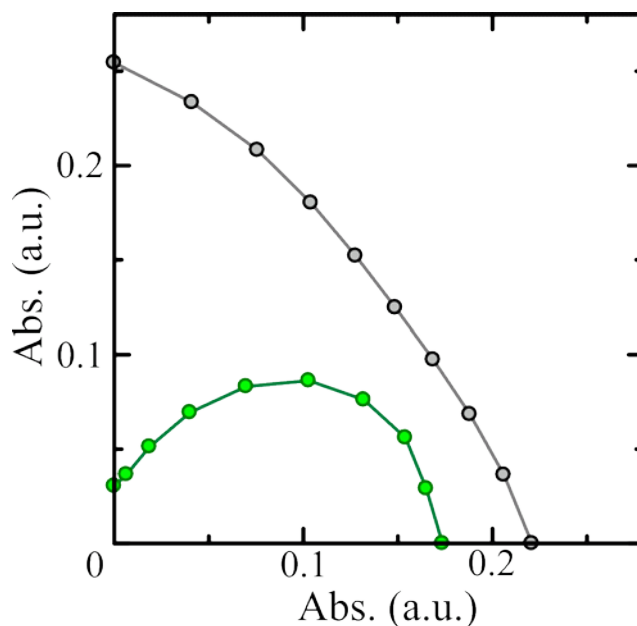


Fig. 8. Peak intensity distribution as a function of polarized angle plotted on the  $x$ - $y$  plane.  $x$ -axis is defined as the orientation direction of the bottom layer. Green and gray plots indicate the bottom (single-layer) film and the orthogonally-coated (double-layer) film, respectively.

Orthogonal coating of conjugated polymers is also the interest counter-process having technological potential in the area of anisotropic opto-electronics. Mismatch of orientation direction consisted of homo-polymer reduces the uniaxial anisotropy. Figure 8 shows the distribution of peak absorption intensity of the films as a function of polarized angle mapped on the  $x$ - $y$  plane. Although the orthogonally double-layered film represents circular trace on the  $x$ - $y$  plane like a non-oriented film but it is not a perfect circle.

These characteristics illustrates that both of the over- and under-layers maintains their orientation morphologies. The absorption spectra of this double-layer film still show vibronic profile unlike a spin-coated one. Concerning the good conservation of the film morphologies in orthogonal coating, each layer maintains the vibronic structure as discussed above. This indicates that we can prepare a non-oriented NR-P3HT film consisted of well-stretched polymer main-chains by the oriented multi-layer coatings into various direction. This possibly provides some unique functions to organic devices.

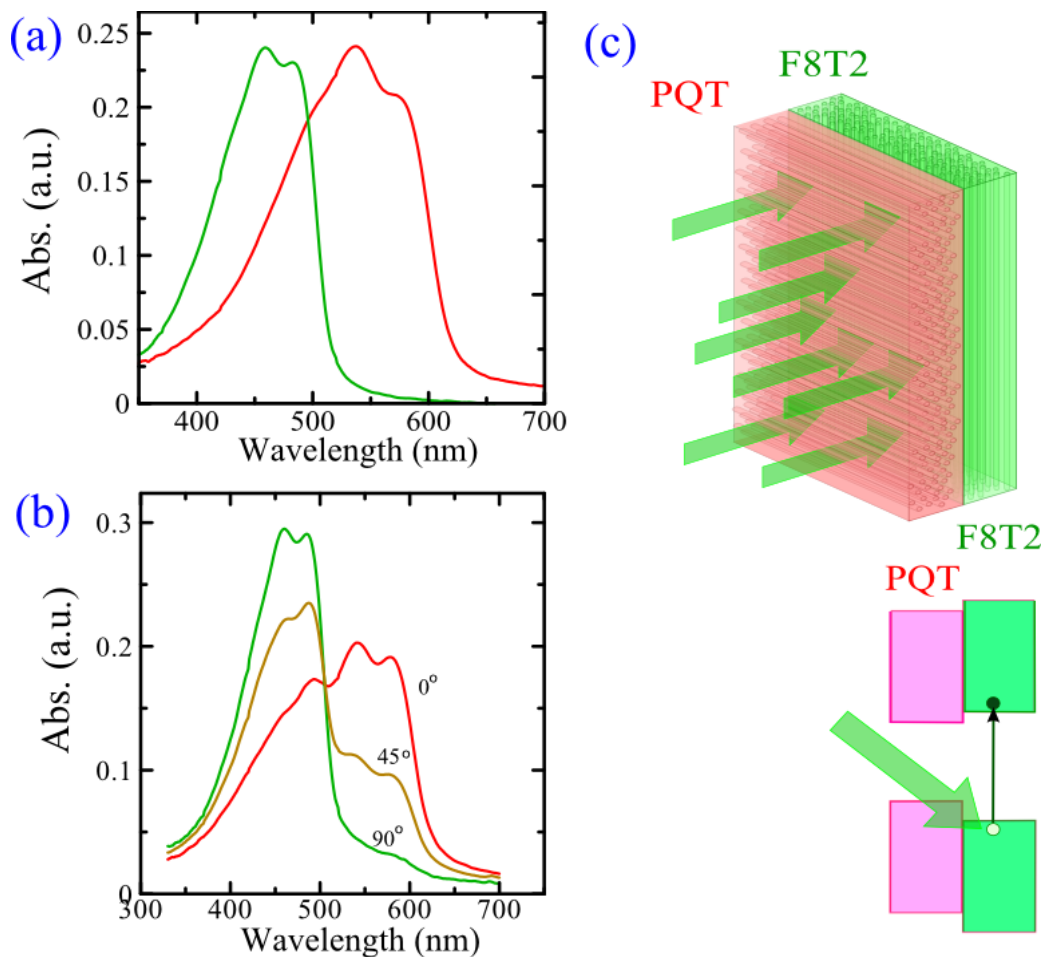


Fig. 9. (a) Absorption spectra of individual FTM films of PQT (red) and F8T2 (green), (b) Polarized electronic absorption spectra of an orthogonally-coated (double-layer) film consisted of oriented PQT and F8T2. The values inside represents the polarized angle based on the PQT orientation. (c) Schematic illustration of the polarized-monochromatic (about 480 nm) light illumination parallel to the F8T2 orientation.

To clarify the orthogonal coatings and its implications on the optical characteristics, we have chosen two different  $\pi$ -conjugated polymers viz. PQT and F8T2. It has been already reported that the main optical absorption-bands of PQT and F8T2 are located around 450-600 nm [43] and 400-500 nm [44], respectively as shown in Fig. 9 (a). In addition both of these polymers can be well-oriented by dynamic-FTM [12]. Orthogonal double-layer has been prepared by over-coating of an oriented F8T2 film onto the oriented PQT film. Owing to the relative mismatch in absorption maxima, we can easily find the changes in the spectral profile as a function of the

polarization angle as shown in the Fig. 9 (b). Relatively strong vibronic modes were still maintained in both the oriented PQT and F8T2 layer indicating their extended  $\pi$ -conjugation length of both layers. This also represents less-interference on the film-morphologies in both the under- as well as the over-layers even after orthogonal over-coating. Observed polarized-angle dependence in the film spectra implies that the polarized-light can pump a proper inner-layer even though the illuminated surface is covered by a low-bandgap material like as schematically illustrated in Fig. 9 (c). The layer-by-layer coating technologies of oriented  $\pi$ -conjugated polymers enable us to explore anisotropic electronics with oriented multi-layer architecture.

## 4. Conclusion

A variety of multi-layer coatings consisted of oriented conjugated polymer-films by dynamic-FTM have been successfully demonstrated. It has been clearly shown that it is possible to conduct parallel coatings of oriented NR-P3HT films while preserving the macromolecular orientation as well as the anisotropy. Multi-layered parallel-coating enables us to prepare uniaxially oriented films with variable thickness utilizing oriented NR-P3HT films. Polarized FT-IR analysis as well as in-plane X-ray analysis using GIXD has been successfully carried out using an oriented thick film prepared by parallel coatings under dynamic FTM. Orthogonal double-coatings consisted of homo-polymer (NR-P3HT) as well as hetero-polymer (PQT/F8T2) has been also demonstrated utilizing polarized electronic absorption spectra. These results suggest unique usage of the oriented multi-layer structure functionalized by their anisotropic architecture.

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## References

1. J.-F. Chang, B. Sun, D.W. Breiby, M.M. Nielsen, T.I. Sölling, M. Giles, I. McCulloch, H. Sirringhaus, Enhanced mobility of poly(3-hexylthiophene) transistors by spin-coating from high-boiling-point solvents, *Chem. Mater.* 16 (2004) 4772–4776.
2. H. Yang, S.W. LeFevre, C.Y. Ryu, Z. Bao, Solubility-driven thin film structures of regioregular poly(3-hexylthiophene) using volatile solvents, *Appl. Phys. Lett.* 90 (2007) 172116.
3. J. Noh, S. Jeong, J.-Y. Lee, Ultrafast formation of air-processable and high quality polymer films on an aqueous substrate, *Nat. Commun.* 7 (2016) 12374.
4. X.L. Chen, A.J. Lovinger, Z. Bao, J. Sapjeta, Morphological and transistor studies of organic molecular semiconductors with anisotropic electrical characteristics, *Chem. Mater.* 13 (2001) 1341–1348.
5. M. Pandey, S. Nagamatsu, S.S. Pandey, S. Hayase, W. Takashima, Enhancement of carrier mobility along with anisotropic transport in non-regiocontrolled poly(3-hexylthiophene) films processed by floating film transfer method, *Org. Electron.* 38 (2016) 115–120.
6. M. Pandey, S.S. Pandey, S. Nagamatsu, S. Hayase, W. Takashima, Solvent driven performance in thin floating-films of PBTTT for organic field effect transistor: role of macroscopic orientation, *Org. Electron.* 43 (2017) 240–246.
7. X. Xue, G. Chandler, X. Zhang, J.R. Kline, Z. Fei, M. Heeney, P.J. Diemer, O.D. Jurchescu, B.T. O'Connor, Oriented liquid crystalline polymer semiconductor films with large ordered domains, *ACS Appl. Mater. Interfaces* 7 (2015) 26726–26734.

8. Y. Shirota, Photo- and electroactive amorphous molecular materials-molecular design, synthesis, reactions, properties and applications, *J. Mater. Chem.* 15 (2005) 75-93.
9. H. Sirringhaus, P.J. Brown, R.H. Friend, Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, *Nature* 401 (1999) 685-688.
10. M.J. Lee, D. Gupta, N. Zhao, M. Heeney, I. McCullough, H. Sirringhaus, Anisotropy of charge transport in a uniaxially aligned and chain-extended high-mobility, conjugated polymer semiconductor, *Adv. Funct. Mater.* 21 (2011) 932–940.
11. T. Morita, V. Singh, S. Nagamatsu, S. Oku, W. Takashima, K. Kaneto, Enhancement of transport characteristics in poly(3-hexylthiophene) films deposited with floating film transfer method, *Appl. Phys. Exp.* (2009) 111502.
12. A. Dauendorffer, R.K. Pandey, S. Miyajima, S. Nagamatsu, R. Prakash, W. Takashima, S. Hayase, K. Kaneto, Fabrication of large-scale drop-cast films of  $\pi$ -conjugated polymers with Floating-film Transfer Method, *Trans. Mat. Res. Soc. Jpn.* 38 (2013) 305-308.
13. M. Pandey, S.S. Pandey, S. Nagamatsu, S. Hayase, W. Takashima, Influence of backbone structure on orientation of conjugated polymers in the dynamic casting of thin floating-films, *Thin Solid Films*, 619 (2016) 125-130.
14. H. Zhu, M. Mitsuishi, T. Miyashita, Facile preparation of highly oriented poly(vinylidene fluoride) langmuir-blodgett nanofilms assisted by amphiphilic polymer nanosheets, *Macromolecules* 45 (2012) 9076-9084.
15. S. Nagano, S. Kodama, T. Seki, Ideal spread monolayer and multilayer formation of fully hydrophobic polythiophenes via liquid crystal hybridization on water, *Langmuir* (2008) 10498-10504.



16. M. Brinkmann, L. Hartmann, L. Biniek, K. Tremel, N. Kayunkid, Orienting semi-conducting  $\pi$ -conjugated polymers, *Macromol. Rapid. Commun.* 35 (2014) 9-26.
17. L. Biniek, N. Leclerc, T. Heiser, R. Bechara, M. Brinkmann, Large scale alignment and charge transport anisotropy of pBTTT films oriented by high temperature rubbing, *Macromolecules* 46 (2013) 4012-4023.
18. S. Nagamatsu, W. Takashima, K. Kaneto, Y. Yoshida, N. Tanigaki, K. Yase, K. Omote, Backbone arrangement in "friction-transferred" regioregular poly(3-alkylthiophene)s, *Macromolecules* 36 (2003) 5252-5257.
19. D.M. DeLongchamp, R.J. Kline, Y. Jung, D.S. Germack, E.K. Lin, A.J. Moad, L.J. Richter, M.F. Toney, M. Heeney, I. McCulloch, Controlling the orientation of terraced nanoscale "Ribbons" of a poly(thiophene) semiconductor, *ACS Nano* 3 (2009) 780-787.
20. Y.J. Cheng, S.H. Yang, C.S. Hsu, Synthesis of conjugated polymers for organic solar cell applications, *Chem. Rev.* 109 (2009) 5868-5923.
21. A. Facchetti,  $\pi$ -conjugated polymers for organic electronics and photovoltaic cell applications, *Chem. Mater.* 23 (2011) 733-758.
22. A. Wang, H. Dong, W. Hu, Y. Liu, Semiconducting  $\pi$ -conjugated systems in field-effect transistors: A material odyssey of organic electronics, *Chem. Rev.* 112 (2012) 2208-2267.
23. T. Morita, V. Singh, S. Oku, S. Nagamatsu, W. Takashima, S. Hayase, K. Kaneto, Ambipolar transport in bilayer organic field-effect transistor based on poly(3-hexylthiophene) and fullerene derivatives, *Jpn. J. Appl. Phys.* 49 (2010) 1-5 041601.
24. A. Dauendorffer, S. Miyajima, S. Nagamatsu, W. Takashima, S. Hayase, K. Kaneto, One-step deposition of self-oriented beta-phase polyfluorene thin films for polarized polymer light-emitting diodes, *Appl. Phys. Exp.* 5 (2012) 1-3 092101.

25. R. Sugimoto, S. Takeda, H.B. Gu, K. Yoshino, Preparation of soluble polythiophene derivatives utilizing transition metal halides as catalysts and their property, *Chem. Express.* 1 (1986) 635-638.
26. S. Amou, O. Haba, K. Shirato, T. Hayakawa, M. Ueda, K. Takeuchi, M. Asai, Head-to-tail regioregularity of poly(3-hexylthiophene) in oxidative coupling polymerization with FeCl<sub>3</sub>, *J. Polym. Sci. Polym. Chem.* 37 (1999) 1943-1948.
27. B.S. Ong, Y. Wu, P. Liu, S. Gardner, High-performance semiconducting polythiophenes for organic thin-film transistors, *J. Am. Chem. Soc.* 126 (2004) 3378-3379.
28. E. Lim, B.J. Jung, H.K. Shim, Synthesis and characterization of a new light-emitting fluorine-thieno[3,2-b]thiophene-based conjugated copolymer, *Macromolecules* 36 (2003) 4288-4293.
29. M. Pandey, S. Nagamatsu, S.S. Pandey, S. Hayase, W. Takashima, Orientation characteristics of non-regiocontrolled poly(3-hexylthiophene) film by FTM on various liquid substrates, *J. Phys: Conf. Ser.* 704 (2016) 012005.
30. M. Pandey, S.S. Pandey, S. Nagamatsu, S. Hayase, W. Takashima, Controlling factors for orientation of conjugated polymer films in dynamic floating-film transfer method, *J. Nanosci. Nanotechnol.* 17 (2017) 1915-1922.
31. T. Chen, X. Wu, R.D. Rieke, Regiocontrolled synthesis of poly(3-alkylthiophenes) mediated by Rieke Zinc: their characterization and solid-state properties, *J. Am. Chem. Soc.* (1995) 233-244.
32. C. Yang, F.P. Orfino, S. Holdcroft, A phenomenological model for predicting thermochromism of regioregular and nonregioregular poly(3-alkylthiophenes), *Macromolecules* 29 (1996) 6510-6517.

33. R.J. Kline, M.D. McGehee, E.N. Kadnikova, J. Liu, J.M.J. Frechet, M.F. Toney, Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight, *Macromolecules* 38 (2005) 3312-3319.
34. S.S. Pandey, W. Takashima, S. Nagamatsu, T. Endo, M. Rikukawa, K. Kaneto, Regioregularity vs regiorandomness: Effect on photocarrier transport in poly(3-hexylthiophene), *Jpn. J. Appl. Phys.* 39 (2000) L94-97.
35. L. Hartmann, K. Tremel, S. Uttiya, E. Crossland, S. Ludwigs, N. Kayunkid, C. Vergnat, M. Brinkmann, 2D versus 3D crystalline order in thin films of regioregular poly(3-hexylthiophene) oriented by mechanical rubbing and epitaxy, *Adv Func Mater* 21 (2011) 4047-4057.
36. W. Takashima, S.S. Pandey, T. Endo, M. Rikukawa, N. Tanigaki, Y. Yoshida, K. Yase, K. Kaneto, Photocarrier transports related to the morphology of regioregular poly(3-hexylthiophene) films, *Thin Solid Films* 393 (2001) 334-342.
37. S. Hotta, M. Soga, N. Sonoda, Infrared dichroic studies of polythiophenes, *J. Phys. Chem.* 93 (1989) 4994-4998.
38. G. Louarn, M. Trznadel, J.P. Buisson, J. Laska, A. Pron, M. Lapkowski, S. Lefrant, Raman spectroscopic studies of regioregular poly(3-alkylthiophenes), *J. Phys. Chem.* 100 (1996) 12532-12539.
39. Y. Furukawa, M. Akimoto, I. Harada, Vibrational key bands and electrical conductivity of polythiophene, *Synth. Met.* 18 (1987) 151-156.
40. G. Louarn, J.P. Buisson, S. Lefrant, D. Fichou, Vibrational studies of a series of  $\alpha$ -oligothiophenes as model system of polythiophene, *J. Phys. Chem.* 99 (1995) 11399-11404.

41. K. Tashiro, K. Ono, Y. Minagawa, M. Kobayashi, T. Kawai, K. Yoshino, Structure and thermochromic solid-state phase transition of poly(3-alkylthiophene), J. Polym. Sci. Polym. Phys. 29 (1991) 1223-1233.
42. G. Gustafsson, O. Inganas, H. Osterholm, J. Laakso, X-ray diffraction and infra-red spectroscopy studies of oriented poly(3-alkylthiophenes), Polymer 32 (1991) 1574-1580.
43. B.S. Ong, Y. Wu, P. Liu, S. Gardner, Structurally ordered polythiophene nanoparticles for high-performance organic thin-film transistors, Adv. Mater. 17 (2005) 1141-1144.
44. A. Dauendorffer, S. Nagamatsu, W. Takashima, K. Kaneto, Optical and Transport Anisotropy in poly(9,9'-dioctyl-fluorene-alt-bithiophene) Films Prepared by Floating Film Transfer Method, Jpn. J. Appl. Phys. 51 (2012) 055802.